

## APPENDIX

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## Ethene/Propene Copolymerization from Metallocene-Based Catalytic Systems: Role of the Alumoxane

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**ABSTRACT:** Ethene/propene copolymerizations were performed with a catalytic system composed of a metallocene and an alumoxane. The role played by the alumoxane was investigated by comparing the effects of three different compounds: poly(methylalumoxane) (MAO), tetraisobutylalumoxane (TIBAO), and tetraisoctylalumoxane (TIOAO). A thorough comparison was performed using *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride (*r*-EBTHIZrCl<sub>2</sub>) as the metallocene. Further data were obtained with isopropylidenebis(3-*t*-butyl-cyclopentadienyl)zirconium dichloride (*r*-Me<sub>2</sub>C(3-*t*-BuCp)<sub>2</sub>ZrCl<sub>2</sub>) and with dimethylsilylenebisfluorenylzirconium dichloride (Me<sub>2</sub>SiFlu<sub>2</sub>ZrCl<sub>2</sub>). Main parameters of copolymerization and copolymers were determined. MAO gives rise to higher polymerization activities and lower molecular masses of the copolymers. A higher productivity is obtained with TIOAO than with TIBAO, whereas these two alumoxanes behave very similarly in determining the copolymer properties. A statistical elaboration allowed to derive the reactivity ratios of the comonomers. The copolymer microstructure is essentially due to the metallocene, even though a MAO-based catalytic system shows a slightly higher reactivity for propene.

### Introduction

Metallocenes had already been used in the 1950s by Natta and Breslow,<sup>1</sup> in combination with aluminum alkyls, as catalysts for ethene polymerization, obtaining very low catalytic activity.

A dramatic upsurge of the catalytic activity was obtained by Sinn and Kaminsky, in the early 1980s, by using a metallocene in combination with poly(methylalumoxane) (MAO).<sup>2</sup> MAO, combined with a metallocene, is able to give rise to highly active catalytic systems for ethene, 1-olefins, cycloolefins, and dienes homo and copolymerizations.<sup>3,4</sup> The discovery of MAO started a huge research activity, in both the academic and industrial worlds, to design on one hand, new metallocenes structures and to identify, on the other hand, new cocatalysts, alternative to MAO.

Boron compounds, combined with metallocenes were proved able to promote homo- and copolymerizations,<sup>5</sup> with a catalytic activity comparable to the MAO-based one.

Montell scientists have discovered and developed cocatalysts based on AlR<sub>3</sub> compounds, where R is an alkyl or aryl radical, and H<sub>2</sub>O.<sup>6</sup> These cocatalysts are formed by reacting AlR<sub>3</sub> and H<sub>2</sub>O, adopting an Al/H<sub>2</sub>O stoichiometric ratio of 2:1. Different generations of these alumoxanes have been prepared in the last years.<sup>7b,8c,a,f,h,9</sup>

In this work, two alumoxanes alternative to MAO were selected: tetraisobutylalumoxane (TIBAO) and tetraisoctylalumoxane (TIOAO) that arise respectively from the reaction of aluminum trisisobutyl and aluminum tris(2,4,4-trimethylpentyl) with H<sub>2</sub>O. They were compared in ethene/propene copolymerizations promoted by *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride (*r*-EBTHIZrCl<sub>2</sub>). This work was mainly aimed at identifying the role played by a fundamental component of the catalytic system as the alumoxane, in the frame of our research in the field of copolymerization.<sup>7-9</sup> Main copolymerization and copolymer features are reported. A statistical elaboration of the collected data

allowed the obtainment of reactivity ratios of the copolymerization. In addition data for copolymerizations performed with other metallocenes as *rac*-isopropylidenebis(3-*t*-butyl-cyclopentadienyl)zirconium dichloride<sup>10</sup> (*rac*-Me<sub>2</sub>C(3-*t*-BuCp)<sub>2</sub>ZrCl<sub>2</sub>) and dimethylsilylenebisfluorenylzirconium dichloride<sup>11</sup> (Me<sub>2</sub>SiFlu<sub>2</sub>ZrCl<sub>2</sub>) are shown.

### Results and Discussion

Ethene/propene copolymerizations were performed in solution and at low pressure, adopting the experimental conditions carefully described in the Experimental Section, whose selection was thoroughly discussed in a previous manuscript.<sup>7c</sup>

Among these conditions it is worth underlying the use of a good solvent as toluene and of a relatively high polymerization temperature (50 °C), the low monomer conversion, and the low polymer concentration in the polymerization medium.

This method allows us to assume that a homogeneous polymerization solution was obtained and that the comonomer concentration on the catalytic center was reasonably constant. Data and results of the copolymerizations performed with TIBAO, TIOAO, and MAO are reported in Table 1.

The polymerization tests were designed so as to allow a reliable collection and elaboration of polymerization results and copolymer data, and to have a correct determination of the reactivity ratios between the comonomers. The low monomer conversion is a *condicio sine qua non* in the frame of this approach, and it was achieved in this work, as clearly shown in Table 1, through a low productivity of the polymerization tests, obtained by using a low amount of catalytic system. This set of experimental conditions is definitely far from the ideal one to investigate the catalytic activity of the catalytic system. Taking also into account that the tests of Table 1 were not reproduced a number of times, no definite statements are possible on the polymerization

Table 1. Ethene/Propene Copolymerization with  $r$ -(EBTHI)ZrCl<sub>2</sub>/Alumoxane as the Catalytic System<sup>a</sup>

run	alumoxane	E/P <sup>b</sup> (mol/mol)		yield (g)	activity (g <sub>PO</sub> /g <sub>Zr</sub> )	copolymer properties		$(E + P)_{catalyzed}$ <sup>c</sup> (g/g)
		gas phase	liquid phase			ethene <sup>d</sup> (% mol)	IV (dL/g)	
1	TIBAO	0.20	0.048	0.06	500	54.4	nd	590
2		0.65	0.15	0.95	3300	66.2	2.1	30
3		0.82	0.19	1.5	9600	74.2	2.4	21
4		1.06	0.25	2.02	12800	78.8	2.5	16
5		2.17	0.51	2.0	12700	88.0	3.1	16
6	TIOAO	0.072	0.017	0.08	150	23.3	nd	450
7		0.21	0.049	0.10	650	49.1	1.4	340
8		0.38	0.092	0.17	950	64.9	nd	320
9		0.82	0.19	0.30	1900	76.3	2.6	105
10		0.83	0.19	0.48	9100	78.8	2.9	70
11		1.17	0.28	2.2	14000	80.8	3.1	14
12	MAO	2.51	0.59	2.3	15000	88.7	4.2	13
13		0.17	0.059	0.05	300	15.9	0.1	1000
14		0.36	0.086	2.5	15800	52.8	0.4	15
15		0.72	0.17	0.50	3200	66.4	0.8	130
16		1.11	0.26	0.80	8700	72.5	1.1	80
17		2.28	0.55	1.00	11000	86.7	2.3	60
18		0.79	0.18	5.8	36750	65.9	0.4	5
19		2.13	0.52	6.9	43700	80.8	1.0	4

<sup>a</sup> Polymerization conditions: toluene = 100 mL; [Zr] =  $1.6 \times 10^{-6}$  mol/L, except for runs 13 and 15–17 where [Zr] =  $9.5 \times 10^{-6}$  mol/L; Al/Zr = 1000 (mol/mol); T = 50 °C, total pressure = 1.1 atm; flow rate of (E + P) mixture = 1.5 L/min except runs 13 and 15–17 where flow rate were 8.0 L/min; time = 15 min. <sup>b</sup> For the value determinations see Experimental Section. <sup>c</sup> From <sup>13</sup>C NMR analysis. <sup>d</sup> Ratio between the monomers fed to the reactor and those converted into the polymer.

Table 2. Ethene/Propene Copolymerization in Solution with  $r$ -(EBTHI)ZrCl<sub>2</sub>/Alumoxane as the Catalytic System<sup>a</sup>

run	alumoxane	E/P (mol/mol)	liquid phase	t (min)	yield (g)	activity (g <sub>PO</sub> /g <sub>Zr</sub> )	polymer properties	
							ethene (wt %)	IV (dL/g)
20	TIBAO	0.16		59	62	432	63.1	4.6
21	TIOAO	0.16		42	114	660	56.9	3.9
22	MAO	0.16		30	150	930	54.0	2.7

<sup>a</sup> Polymerization conditions:  $\mu$ mol Zr = 1.88; ethene = 44.7 g; propene = 388 g; hexane = 1324 g; Al/Zr = 1000 molar ratio; T = 50 °C.

activity. However it is possible to observe that MAO brings about a higher activity than TIOAO and TIBAO. Moreover, data collected and reproduced with experimental conditions of industrial significance, in aliphatic solvents and at higher monomer concentration, confirm the higher productivity of  $r$ -(EBTHI)ZrCl<sub>2</sub> when combined with MAO and allow one to clearly identify the higher activity of the TIOAO-based system with respect to the TIBAO-based one. Standard tests are in Table 2 as a support to these statements.

A high catalytic activity can affect the correct determination of the relative reactivity of the comonomers, as it appears from the comparison of the results of tests 18 and 19 with the others reported in the same table. Copolymer samples 18 and 19 have a remarkably lower ethene content than samples prepared with much lower catalytic activity and a comparable or even lower ethene concentration in the polymerization bath, such as samples 16 and 17. In fact, even in the absence of remarkable physical limitations, a high catalytic activity, bringing about a high monomer conversion, does not allow one to maintain a constant concentration of the comonomers on the catalytic center, especially of the most reactive one, i.e., ethene. This brings the catalytic system in a starving situation with respect to ethene and leads thus to a reduction of the ethene content in the copolymer. In this case the values determined for the reactivity ratios of the comonomers are therefore incorrect and the relative reactivity of ethene is underestimated.

From the intrinsic viscosities data, reported in Table 1, it appears that copolymers with higher molecular

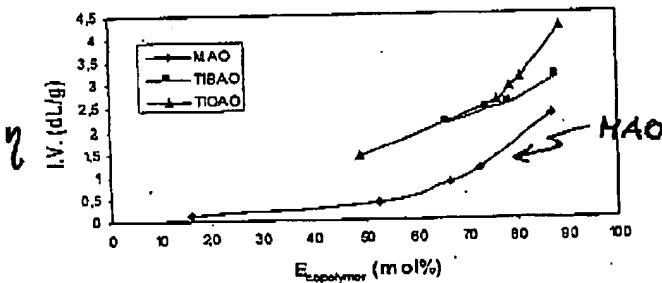


Figure 1. Intrinsic viscosity (dL/g) vs ethene content for ethene/propene copolymers prepared with  $r$ -(EBTHI)ZrCl<sub>2</sub> and TIBAO (■), TIOAO (▲), and MAO (◆) as catalytic system.

mass are prepared with TIOAO and TIBAO, whereas lower molecular masses are obtained with MAO. Figure 1, built with the data of Table 1, shows that the intrinsic viscosity of the copolymers increases as the ethene content increases, following a trend already reported for different types of metallocenes,<sup>9</sup> which is also typical of the ethene/propene copolymers produced with other catalytic systems.<sup>12</sup> It is interesting to observe that the slope of the lines described by the different alumoxanes, TIOAO, TIBAO, and MAO, are pretty similar. The typical molecular mass distribution of metallocene-based polymers was shown by the GPC analysis: samples 2, 8, 9, 14, and 16 have  $M_w/M_n$  values ranging from 2 to 2.3, to indicate that the three alumoxanes give identically rise to single center catalytic systems. This was also confirmed by fractionating the copolymers of Table 2, with a method<sup>7,13</sup> that allows one to isolate fractions

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Table 3. Fractionation of Two Ethene/Propene Copolymers Obtained with *r*-(EBTHD)ZrCl<sub>2</sub> as Catalyst and TIBAO (Sample 20<sup>a</sup>) or TIOAO (Sample 21<sup>a</sup>) as Cocatalysts

fraction	solvent(s) <sup>b</sup> (vol/vol)	wt % of the fraction		ethene (wt %)		IV (dL/g)	
		sample 20	sample 21 <sup>c</sup>	sample 20	sample 21	sample 20	sample 21
raw polymer				63.1	56.9	4.6	3.9
1	ether	2.7	15.7	60.1	51.7	1.1	1.7
2	ether/hexane = 95/5	4.1	18.2	59.9	53.2	1.5	2.7
3	ether/hexane = 90/10	10.4	24.6	60.8	56.7	2.3	3.5
4	ether/hexane = 80/20	70.9	37.2	62.9	61.0	4.8	5.0
5	none <sup>d</sup>	11.9	4.1	64.4	63.9	7.3	7.5
average values		100.0	99.8	62.7	57.1	3.6	3.8

<sup>a</sup> Samples have the numbers of the corresponding runs. <sup>b</sup> Ether = diethyl ether. <sup>c</sup> 0.2% of this copolymer was extracted with ether/acetone = 80/20 (vol/vol). <sup>d</sup> Residual fraction.

Table 4. <sup>13</sup>C-NMR Triad Distributions for Ethene/Propene Copolymers Obtained with *r*-(EBTHD)ZrCl<sub>2</sub>/Alumoxane as the Catalytic System

sample <sup>a</sup>	cocatalyst	E/P <sup>b</sup> (mol/mol)	E <sub>copolymer</sub> <sup>c</sup> (% mol)	triads					
				PPP	PPE	EPE	PEP	PEE	EEE
1	TIBAO	0.048	54.4	13.1	13.9	18.6	17.8	24.7	11.9
2		0.15	76.0	2.2	5.2	17.6	5.7	28.8	40.5
3		0.19	74.2	0.0	6.5	19.3	2.4	25.5	46.3
4		0.25	78.8	0.9	4.4	15.9	6.1	28.8	43.9
5		0.51	88.0	0.0	2.5	9.5	0.0	21.1	66.9
6	TIOAO	0.017	23.3	49.3	20.8	6.6	14.0	7.6	1.7
7		0.049	49.0	15.8	16.8	18.4	17.1	22.0	9.9
8		0.092	64.8	4.6	10.1	20.5	9.6	29.3	25.9
9		0.19	76.3	1.3	4.6	17.8	5.2	28.3	42.8
10		0.19 <sub>e</sub>	78.8	0.5	4.3	16.4	5.1	27.8	45.9
11		0.28	80.8	1.0	3.7	14.5	4.6	27.6	48.6
12		0.59	88.7	0.0	2.1	9.2	1.6	19.0	68.1
13	MAO	0.029	15.9	64.1	17.8	2.7	10.0	5.5	0.4
14		0.086	52.8	11.3	16.0	19.9	14.3	25.1	13.4
15		0.17	65.4	4.4	8.9	20.3	8.2	28.2	30.0
16		0.26	72.5	2.7	7.1	17.7	6.9	29.5	36.1
17		0.54	86.8	0.7	2.1	10.4	2.2	21.5	63.1
18		0.18	65.9	3.2	10.1	20.8	9.8	32.4	23.7
19		0.52	80.9	0.0	3.7	15.4	4.0	26.9	50.0

<sup>a</sup> Samples have the number of the corresponding runs. <sup>b</sup> Feed ratio in liquid phase. <sup>c</sup> Copolymer composition obtained from triad distribution as E = EEE + EEP + PEP.

having different chemical compositions, if there are any in the copolymer. Results of the fractionations are reported in Table 3 and clearly show the narrow chemical composition distribution of a copolymer prepared from a metallocene-based catalytic system activated by an alumoxane other than MAO.

The microstructure of the copolymers was fully characterized through <sup>13</sup>C NMR analysis. Triad distributions are in Table 4 for TIBAO-, TIOAO-, and MAO-based samples, respectively. These data were elaborated through a method, already reported in previous manuscripts,<sup>7c,9</sup> that allows one to determine the statistical model suitable to describe the copolymerization as well as the reactivity ratios between the comonomers. A second-order Markov model was found to allow the best fit of the experimental data. Graphics are reported in Figure 2 for the TIOAO-based samples, to show the comparison between the first and the second-order Markov model for fitting the experimental distribution of the P centered triads. The P centered triads were selected to indicate that a second-order Markov model has to be adopted to justify, in particular, the amount of this type of sequences. This statistical model was already adopted by Fink<sup>14</sup> to describe copolymerizations promoted by *r*-Me<sub>2</sub>SiInd<sub>2</sub>ZrCl<sub>2</sub> and *r*-Me<sub>2</sub>CCpFluZrCl<sub>2</sub> as the metallocenes. We have already commented on the selection of a second-order Markov model for copolymerizations promoted by metallocenes of the type *r*-XInd<sub>2</sub>ZrCl<sub>2</sub> or *r*-X(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> where X = ethylene

or dimethylsilylene.<sup>7a,9</sup> However, a mechanistic interpretation of these results is not yet available. Hence, it is only possible to say, at the present stage of the research, that the selection of a statistical model to describe a copolymerization is essentially justified by the optimum fit with the experimental data. As a consequence of the adoption of the second-order Markov model, the following reactivity ratios can be derived:

$$r_{11} = k_{111}/k_{112}$$

$$r_{21} = k_{211}/k_{212}$$

$$r_{22} = k_{222}/k_{221}$$

$$r_{12} = k_{122}/k_{121}$$

In Table 5, the values obtained for TIBAO-, TIOAO-, and MAO-based copolymerizations are reported. It can be commented that TIBAO and TIOAO give rise to almost identical reactivity ratios. For the MAO based catalytic system, a higher reactivity for propene seems to be indicated by the lower  $r_{11}$  and  $r_{21}$  values and by the higher  $r_{22}$  and  $r_{12}$  values. However, one has to say that the difference with the values obtained with TIBAO and TIOAO is subtle, and in conclusion, all the reactivity ratios lie in a pretty narrow range. The values of  $r_1$  and  $r_2$  reported in the literature for metallocene-based copolymerizations cover a much broader latitude. Therefore, it is possible to say that the results of the

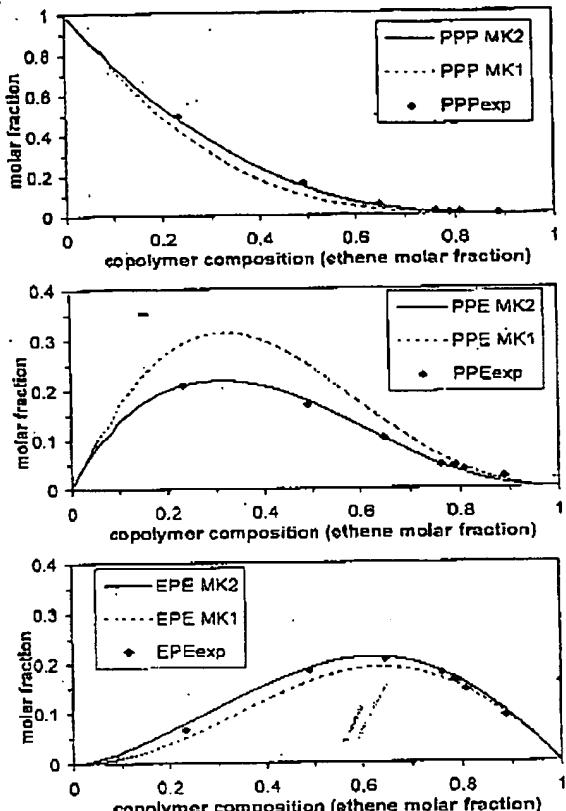


Figure 2. Molar fraction of triads centered on propene vs copolymer composition for ethene/propene copolymers prepared with  $r$ -(EBTHI) $ZrCl_2$ /TIOAO as catalytic system. Comparison of first- and second-order Markovian models (MK1 and MK2 respectively).

Table 6. Reactivity Ratios for Ethene/Propene Copolymerizations with  $r$ -(EBTHI) $ZrCl_2$ /Alumoxane as the Catalytic System<sup>a</sup>

alumoxane	reactivity ratios <sup>b</sup>			
	$r_{11}$	$r_{22}$	$r_{21}$	$r_{12}$
TIBAO	$15 \pm 1$	$0.08 \pm 0.03$	$16 \pm 4$	$0.020 \pm 0.006$
TIOAO	$14.8 \pm 0.8$	$0.082 \pm 0.008$	$15 \pm 2$	$0.024 \pm 0.003$
MAO	$11 \pm 1$	$0.29 \pm 0.07$	$10 \pm 3$	$0.04 \pm 0.01$

<sup>a</sup> The experimental conditions are indicated in Table 1 for TIBAO-, TIOAO-, and MAO-based tests, respectively. <sup>b</sup> Calculated with the method described in refs 7c and 9 using a 2nd order Markovian model.

copolymerizations described in this manuscript can be reasonably correlated with the structure of the metallocene and that the cocatalyst plays a minor role. To further investigate this aspect, a cocatalytic system other than an alumoxane, composed of a boron compound and Al(isobutyl)<sub>3</sub>, was used, in combination with  $r$ -EBTHI $ZrCl_2$ , in ethene/propene copolymerizations performed under the same experimental conditions. A careful rationalization of the collected results is in progress. However, from the available data, the reactivity ratios can be calculated through the same statistical method:  $r_{11} = 16.6 \pm 0.6$ ,  $r_{21} = 11.7 \pm 1.0$ ,  $r_{22} = 0.11 \pm 0.01$ , and  $r_{12} = 0.027 \pm 0.03$ .

The values obtained with the boron compound are very similar to those of TIBAO- and TIOAO-based tests

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Table 6. Microstructure of Ethene/Propene Copolymers Obtained with  $r$ -(EBTHI) $ZrCl_2$ /Alumoxane as the Catalytic System

alumoxane	sample <sup>a</sup>	P content in the copolymer (mol %)	PPP/P	iso-index <sup>b</sup>	regioirr <sup>c</sup> (mol %)
TIOAO	6	76.7	0.63	58.2	1.2
MAO	13	84.0	0.75	53.6	0.81

<sup>a</sup> Samples have the numbers of the corresponding runs. <sup>b</sup> Calculated with the following equation: iso-index =  $(T_{pp})_{mm}/[(T_{pp})_{mm} + (T_{pp})_{mm...}]$  (where  $T_{pp} = (CH)_{PP}$ ). <sup>c</sup> Values corresponding to the lower limits calculated according to ref 19.

and fall in the same range described by the three alumoxanes.

The microstructure of the copolymers of Table 1 was also investigated to assess the stereo- and regioregularity of the propene placement. Samples with different propene content, prepared with the three cocatalysts, were analyzed. Results are collected in Table 6 for TIOAO- and MAO-based samples to show that similar values are obtained for both isotacticity (pretty far from 100%) and amount of regioirregularity, and this leads one to exclude a detectable influence of the cocatalyst on these aspects.

Alumoxanes alternative to MAO were studied also in ethene/propene copolymerizations, promoted by metallocenes other than  $r$ -(EBTHI) $ZrCl_2$ . The metallocenes  $Me_2SiFlu_2ZrCl_2$  and  $r$ - $Me_2C(3-t-BuCp)_2ZrCl_2$  were selected for this investigation, as suitable candidates for the preparation of ethene/propene copolymers with almost alternate distribution<sup>2,6,8,9,13</sup> and with long sequences of comonomers,<sup>7,8,14,15</sup> respectively. A detailed discussion of the copolymerizations promoted by these metallocenes, particulary as far as the statistical copolymerization models are concerned, have been already reported<sup>7c</sup> and will be also published in forthcoming manuscripts.<sup>16</sup>

In Tables 7 and 8 polymerizations data as well as copolymer characteristics, in particular the triad distribution and the product of the reactivity ratios, are shown *vis à vis* for MAO- and TIOAO-based tests. These results prove that also in the case of copolymerizations characterized by very different product of reactivity ratios, the copolymer microstructure can be correlated with the metallocene used for the copolymerization rather than with the type of the cocatalyst.

## Experimental Section

**General Procedures and Materials.** All reactions and manipulation were carried out under dry nitrogen atmosphere using the Schlenk tube technique. All the chemicals were stored under nitrogen.

Toluene (Carlo Erba RPE) was deoxygenated by bubbling dry nitrogen, maintained overnight under nitrogen in the presence of  $CaCl_2$ , filtered, refluxed for 8 h over Al(isobutyl)<sub>3</sub>, and finally distilled.

Hexene (Carlo Erba, RPE) was refluxed for 8 h over Al(isobutyl)<sub>3</sub> and distilled.

Polymerization grade ethene and propene were received directly from Montell Ferrara plants. Ethene/propene mixtures were prepared in a 5 L steel cylinder, filled with quantities of the two gases small enough to prevent their condensation.

TIBAO (Witco, 10% w/w in cyclohexane) and MAO (Witco, 10% w/w in toluene) were used without any further treatment.

TIOA was purchased from Witco and used as a 20% (wt/v) solution in hexane.

$r$ -(EBTHI) $ZrCl_2$  was purchased from Witco and analyzed through <sup>1</sup>H NMR to assess its chemical purity.

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Table 7. Ethene/Propene Copolymerizations with a Metallocene/Alumoxane Catalytic System<sup>a</sup>

run	metallocene	alumoxane	E/P (mol/mol)		yield (g)	activity (g <sub>cat</sub> /g <sub>polym</sub> )	copolymer properties		
			gas phase	liquid phase			ethene <sup>b</sup> (% mol)	IV (dL/g)	(E + P) <sub>act</sub> / (E + P) <sub>copolymer</sub> <sup>c</sup>
23	<i>t</i> -Me <sub>2</sub> C(3- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub>	MAO	2.2	0.58	0.5	3440	92.5	0.7	52
		TIOAO	2.2	0.53	0.4	1270	95.2	n.d.	72
25	Me <sub>2</sub> SiFlu <sub>2</sub> ZrCl <sub>2</sub>	MAO	1.9	0.50	0.4	1300	76.2	1.3	72
		TIOAO	2.2	0.53	2.8	8300	71.9	1.2	11

<sup>a</sup> Polymerization conditions: toluene = 100 mL; Al/Zr = 1000 (mol/mol); T = 50 °C; total pressure = 1.1 atm; flow rate of (E + P) mixture = 1.5 L/min; time = 15 min. <sup>b</sup> From <sup>13</sup>C NMR analysis. <sup>c</sup> Weight ratio between the monomers fed to the reactor and those converted into the polymer.

Table 8. <sup>13</sup>C-NMR Triad Distributions and Product of Reactivity Ratios for Ethene/Propene Copolymers Obtained with Metallocene/Alumoxane as the Catalytic System

sample	catalytic system	E/P <sup>b</sup> (mol/mol)	(E) <sub>copolymer</sub> <sup>c</sup> (% mol)	triads						$r_1 r_2^d$
				PPP	PPE	EPE	PEP	PEE	EEE	
23	<i>t</i> -Me <sub>2</sub> C(3- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub> /MAO	0.53	92.5	0.0	2.5	4.9	0.8	10.6	81.2	3.5
24	<i>t</i> -Me <sub>2</sub> C(3- <i>t</i> -Bu-Cp) <sub>2</sub> ZrCl <sub>2</sub> /TIOAO	0.53	95.2	0.0	1.5	3.3	0.0	7.1	88.2	4.7
25	Me <sub>2</sub> SiFlu <sub>2</sub> ZrCl <sub>2</sub> /MAO	0.50	76.2	0.0	1.7	22.0	7.8	30.7	33.3	0.09
26	Me <sub>2</sub> SiFlu <sub>2</sub> ZrCl <sub>2</sub> /TIOAO	0.53	71.9	0.0	2.7	25.4	11.4	33.2	27.3	0.09

<sup>a</sup> Samples have the number of the corresponding runs. <sup>b</sup> Feed ratio in liquid phase. <sup>c</sup> From triad distribution as E = PEP + PEE + EEE. <sup>d</sup> Calculated according to ref 20.

*t*-Me<sub>2</sub>C(3-*t*-Bu-Cp)<sub>2</sub>ZrCl<sub>2</sub> was prepared in Montell following the reported procedure.<sup>10</sup>

Me<sub>2</sub>SiFlu<sub>2</sub>ZrCl<sub>2</sub> was prepared in Montell following the reported procedure.<sup>11</sup>

Preparation of TIOAO. Preparation of TIOAO for the synthesis of sample 3 is reported as an example.

First 1.73 mL of a TIOA solution (1 M in hexane) was added at room temperature to 5 mL of toluene. Then 0.016 mL of H<sub>2</sub>O was added at room temperature with a syringe, and the resulting solution was stirred for 10 min at room temperature.

Determination of the Concentration of the Polymerization Solutions. The vapor-liquid equilibrium for ethene/propene/toluene and ethene/propene/hexane mixtures was estimated from the Redlich Kwong Soave equations. This set of thermodynamic equations was selected on the basis of a comparison with experimental results among those available in Aspen Plus (Release 9), commercialized by Aspen Technology Inc. The concentrations of the comonomers were hence calculated.

Polymerizations. Low-Pressure Polymerizations. Polymerizations were performed at 50 °C, in a 250 mL glass reactor, equipped with a mechanical stirrer, a thermometer, and a pipe for monomer feeding. Preparation of sample 3 is reported as an example. First 100 mL of toluene and 1 mL of MAO solution (1.73 μmol of aluminum) were introduced into the nitrogen-purged reactor, kept in a thermostatic bath. At the polymerization temperature, the monomer mixture was fed with a flow of 1.5 L/min. The composition of the gaseous ethene/propene mixture was determined before and during the test. The adopted conditions were reported to allow the equilibrium between liquid and gaseous phase for the monomers.<sup>12</sup> When the equilibrium pressure (1.1 atm of overpressure obtained through a mercury valve) was reached, 0.7 mg (1.73 μmol) of catalyst, dissolved in 5 mL of toluene in the presence of 1-2 μmol of MAO, was added to start the polymerization. During the polymerization, the temperature was kept within ±1 °C. The polymerization was stopped after 15 min by adding 1 mL of methanol, and the copolymer was recovered by precipitation in methanol/HCl and filtration and finally dried at 50 °C under reduced pressure.

High-Pressure Polymerization. Polymerizations were performed in a 4 L steel autoclave, equipped with a mechanical stirrer, an external jacket for the circulation of a mixture of steam and water to regulate internal temperature, a glass window to have a visual control of the reaction, and valves for the introduction of liquids and gases. Temperature, pressure, and monomer feeding were regulated and controlled by

Preparation of sample 20 is reported as an example.

First 2090 mL of hexane, 42.4 g of ethene, and 395.0 g of propene were introduced into the autoclave at room temperature. The reactor was heated at 50 °C, and a solution prepared by dissolving the metallocene (0.8 mg) in the amount of alumoxane solution (0.372 g of Al) was injected.

During the polymerization, the pressure was kept constant by feeding ethene and the temperature was maintained within ±0.1 °C. A homogeneous polymer solution was formed. Then the reaction was stopped by injecting CO. Monomers and solvent were purged out and the copolymer was recovered by precipitation in acetone and filtration and dried under reduced pressure at 60 °C for 3 h.

Polymer Analysis. Intrinsic viscosities were determined in tetrahydronaphthalene at 135 °C. GPC measurements were performed on a Waters 150-C GPC equipped with TSK columns (Model GM-HXL-HT) with 1,2-dichlorobenzene as solvent, at 135 °C. Monodisperse fractions of polystyrene were used as standards.

Copolymer Fractionation. The fractionation of the copolymers was performed using a sequence of solvents (pure or a mixture) with increasing solubility power, at their boiling point. First 600 mL of the solvent with the lowest solubility power and 6.0 g of polymer were introduced, under nitrogen in a round-bottomed flask, equipped with mechanical stirrer. The mixture was allowed to reflux for 6 h and then to reach room temperature under stirring. The solution was then separated from the unsolved polymer by filtration. The solvent was removed by evaporation at reduced pressure and the recovered polymer was dried at 40 °C for about 12 h at reduced pressure and weighted.

The unsolved polymer was treated in the same way using the solvent with a solubility power higher than the previous one. This procedure was repeated 4-7 times until the unsolved polymer is less than 5% of the initial sample. In this way, fractions with increasing ethene content are separated.

NMR Analysis. <sup>13</sup>C NMR spectra were obtained with Bruker DPX-200 or DPX-400 spectrometers operating respectively at 50.32 and 100.62 MHz in the Fourier transform mode at 120 °C. The peak of the S<sub>66</sub> carbon (nomenclature according to Carman<sup>17</sup>) was used as internal reference ( $\delta$  = 29.9 ppm). The samples were dissolved in 1,1,2,2-tetrachloroethane-d<sub>2</sub> at 120 °C with a 5% w/v concentration. Each spectrum was acquired with a 90° pulse, 12 s of delay between pulses, and CPD (waltz16) to remove <sup>1</sup>H-<sup>13</sup>C coupling. About 5000 transients were stored in 92K data points using a spectral window

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Tried distribution was calculated according to Kakugo.<sup>18</sup> Data for sample 23 were obtained according to ref 7c.

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